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DETAILED MECHANISM OF TOLUENE OXIDATION AND COMPARISON WITH BENZENE

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INTRODUCTION

The importance of aromatic hydrocarbons in today's practical hydrocarbon fuels is well known. This fact has resulted in several new studies of the oxidation and pyrolysis mechanisms of these compounds. A recent review paper[1] has summarized the qualitative knowledge of the mechanism of oxidation of the simplest aromatics, benzene, toluene, and ethyl benzene. In addition, many of the individual reactions in the pyrolysis and oxidation of benzene and toluene have been studied in several papers.[2-8] This information has been used[9] to construct the first detailed mechanism of benzene oxidation. The mechanism was tested using available experimental data on ignition delay times[10] and on temperature and composition profiles measured during benzene oxidation in a highly turbulent reactor.[1] It was found to compute the measured ignition delay times and temperature profile reasonably well and to semiquantitatively reproduce some of the composition profiles.

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In the present work we develop a detailed mechanism for toluene oxidation using the same method as applied previously to the benzene oxidation. Recent information[3-6] on toluene pyrolysis and oxidation reactions was combined with the detailed benzene oxidation mechanism. The resulting mechanism was used to compute experimentally measured ignition-delay times[10] for shock-heated toluene-oxygen-argon mixtures and composition profiles for two toluene-oxygen-nitrogen mixtures in a turbulent flow reactor.[3] Most of the rate coefficients for the toluene reactions were used at their published literature values. Only those rate constants with large uncertainties were adjusted. The reactions controlling the ignition process and the profiles of various species concentrations were determined by an extensive sensitivity analysis using the new NASA Lewis Research Center chemical kinetics and sensitivity analysis code.[11,12]

In the sections that follow we present comparisons of computed and experimental results and describe the sensitivity analysis results.

TOLUENE OXIDATION MECHANISM

The qualitative toluene oxidation and pyrolysis paths already outlined[1] have been used along with the results of recent experimental work[3-6] to write the following initiation and chain propagation scheme involving toluene and its pyrolysis fragments:

Initiation:

$$C_7H_8 + O_2 \rightleftharpoons C_6H_5CH_2 + HO_2 \qquad (1)$$

$$C_7H_8 \rightleftharpoons C_6H_5CH_2 + H \qquad (2)$$

$$C_7H_8 \rightleftharpoons C_6H_5 + CH_3 \qquad (3)$$

Chain propagation:

$$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3 \qquad (4)$$

$$H + C_7H_8 \rightleftharpoons \underset{\text{benzyl}}{C_6H_5CH_2} + H_2 \qquad (5)$$

$$H + C_7H_8 \rightleftharpoons \underset{\substack{\text{methyl}\\ \text{phenyl}}}{C_6H_4CH_3} + H_2 \qquad (6)$$

$$CH_3 + C_7H_8 \rightleftharpoons C_6H_5CH_2 + CH_4 \qquad (7)$$

$$CH_3 + C_7H_8 \rightleftharpoons C_6H_4CH_3 + CH_4 \qquad (8)$$

$$C_6H_4CH_3 \rightleftharpoons C_4H_3 + C_3H_4 \qquad (9)$$

$$C_6H_4CH_3 \rightleftharpoons C_3H_3 + 2\ C_2H_2 \qquad (10)$$

$$C_6H_5CH_2 \rightleftharpoons C_3H_3 + 2\ C_2H_2 \qquad (11)$$

$$CH_3 + C_6H_6 \rightleftharpoons CH_4 + C_6H_5 \tag{12}$$

$$C_3H_4 + M \rightleftharpoons C_3H_3 + H + M \tag{13}$$

$$H + C_3H_4 \rightleftharpoons C_3H_3 + H_2 \tag{14}$$

$$O + C_7H_8 \rightleftharpoons \underset{\text{cresols}}{OHC_7H_7} \tag{15}$$

$$OH + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2O \tag{16}$$

$$C_6H_5CH_2 + O \rightleftharpoons C_6H_5CHO + H \tag{17}$$

$$C_6H_5CH_2 + O_2 \rightleftharpoons \underset{\text{benzoxy}}{C_7H_7O} + O \tag{18}$$

$$OH + C_7H_7OH \rightleftharpoons C_7H_7O + H_2O \tag{19}$$

$$C_6H_5CH_2 + OH + M \rightleftharpoons \underset{\substack{\text{benzyl}\\ \text{alcohol}}}{C_7H_7OH} + M \tag{20}$$

$$C_6H_5CH_2 + HO_2 \rightleftharpoons C_7H_7O + OH \tag{21}$$

$$C_7H_7O \rightleftharpoons C_6H_5CHO + H \tag{22}$$

$$C_6H_5CHO \rightleftharpoons C_6H_5 + HCO \tag{23}$$

$$2\ C_6H_5CH_2 \rightleftharpoons \underset{\text{bibenzyl}}{C_{14}H_{14}} \tag{24}$$

$$OHC_7H_7 + H_2 \rightleftharpoons C_6H_5OH + CH_4 \tag{25}$$

$$2\ C_6H_5 \rightleftharpoons C_{12}H_{10} \tag{26}$$

$$C_6H_5CHO + O_2 \rightleftharpoons C_6H_5CO + HO_2 \tag{27}$$

$$C_6H_5CHO + OH \rightleftharpoons C_6H_5CO + H_2O \tag{28}$$

$$C_6H_5CHO + HO_2 \rightleftharpoons C_6H_5CO + H_2O_2 \tag{29}$$

$$C_6H_5CO \rightleftharpoons C_6H_5 + CO \tag{30}$$

The species OHC_7H_7 represents a composite mixture of ortho, para, and meta cresols. The reactions above were combined with the benzene oxidation and combustion mechanism developed previously[9] to give a system of 143 reactions among 46 species. As in the case of benzene oxidation, one reaction from the hydrogen-oxygen system was found to be important in the toluene oxidation mechanism, namely:

$$H + O_2 \rightleftharpoons OH + O \tag{47}$$

This reaction is important in both initiation and chain propagation. A listing of the significant toluene and benzene initiation and chain reactions (plus the $H + O_2 \rightleftharpoons OH + O$ reaction) is given in Table I along with the rate coefficients used. All other reactions used in the computations have been given in our previous work.[9] Rate coefficients for the pyrolysis reactions 3, 4, and 6 to 14 were all taken unchanged from the work of Pamidimukkala et. al.[4] Selection of the rate coefficients used for reactions 2, 5, and the oxidation reactions is described below.

SENSITIVITY ANALYSIS STUDY

We used the method described previously[9] to compute normalized sensitivity coefficients of species concentrations, temperature, and pressure with respect to the parameters of the modified Arrhenius rate coefficient expression, $k = AT^n \exp(-E/RT)$, for each reaction. Sensitivities with respect to the preexponential factors, A, of several benzene and toluene reactions are listed in Tables II and III. It should be noted that sensitivity coefficients with respect to the activation energy, E, are approximately equal in sign and magnitude to those for A under all conditions studied. Ignition delay times[10] were measured from pressure-time traces by a method described below. Shown in Table II are pressure sensitivity coefficients for ignitions of two shock-heated toluene-oxygen-argon mixtures. These are the lowest temperature lean mixture and a high temperature stoichiometric mixture. As shown in the table the reaction of toluene with molecular oxygen (reaction 1) and that of hydroperoxyl radical with benzyl radical (reaction 21) are the most important reactions which control the ignition delay time. Also showing significant sensitivity here are the $H + O_2$ chain branching reaction (reaction 47), oxygen atom plus benzyl radical (reaction 17), and two important benzene oxidation reactions of phenyl and cyclopentadienyl radical by molecular oxygen (reactions 38 and 45). The latter are of equal or greater importance than the oxygen atom plus benzyl reaction in both of the mixtures shown in Table II. The direct reaction of benzyl radical with molecular oxygen is insignificant, in direct contrast to the dominance of the phenyl plus oxygen reaction in the oxidation of benzene[9] caused by its much higher rate coefficient and molar rate. The conclusions drawn from Table II agree closely with the findings of previous investigators[3] that radical-radical reactions should be important in the toluene oxidation and that the low rate of the benzyl-molecular oxygen reaction makes it unimportant. We note that reaction 5, though unimportant for the low temperature mixture, becomes as sensitive as reaction 17 in the higher temperature stoichiometric mixture.

Table III presents sensitivity coefficients of several species concentrations for the oxidation of a lean toluene mixture in a turbulent reactor. These results show that the five reactions important for ignition delay times are also important in determining the concentration profiles of several species. In addition, reactions 4, 5, 15, 16, 20, and 29 have strong effects on the cresols, benzene, phenol, benzyl alcohol, and bibenzyl profiles. The phenyl and cyclopentadienyl oxidation reactions 38 and 45 have a moderate effect on the concentration profiles of phenol and carbon monoxide. As only an estimate of the rate coefficient of the highly sensitive reaction between toluene and molecular oxygen exists,[8] we consider this reaction to be an adjustable parameter to be used in matching the computations to the experimental results.

The following procedure was used to obtain the best possible matching to the experimental data: Reaction 21 was set within 20 percent of its collision theory estimate.[3] The activation energy and preexponential factor for reaction 1 were adjusted to closely predict the high-temperature (1343 to 1600 K) experimental ignition delay times in argon-diluted mixtures and also give a temperature rise of no more than 5 K for the two different mixtures in the turbulent flow reactor at 1180 K. In these computations the rate coefficient of the pyrolysis reaction 2 was taken as one half that of reaction 3. This is the ratio given by Pamidimukkala et al.[4] for their lowest temperature of 1600 K and was used without any attempted variation. The rate constant of Robaugh and Tsang[5] was used for reaction 5 because it is a directly measured experimental value and gave the best compromise in attempting to match the highest temperature ignition delay times and some of the turbulent reactor experimental composition profiles. Finally, the rate coefficients of reactions 15 to 30 were either estimated or used at or near their literature estimates to give the best possible agreement with the turbulent flow reactor data. Only those coefficients which had no effect on the computed pressure profiles were changed.

DESCRIPTION OF COMPUTATIONAL PROCEDURE

The same procedures used in our benzene mechanism study[9] were used in this work to model the experimental ignition delay time measurements[10] and the experimental composition profile data[3] that have been published for toluene-oxygen mixtures. Only the important details will be summarized here.

Shock Tube Ignition Experiments

A constant volume batch reaction model was used for the shock-heated mixtures. The reported initial reflected-shock temperature and pressure conditions[10] were recomputed, as described previously,[9] applying a small correction for attenuation of the shock velocity to each data point. As shown by Brabbs and Robertson,[13] all data points with ignition delay times less than 100 μsec were considered inaccurate and eliminated from consideration. Experimental ignition delay time was determined from each experimental pressure versus time curve as the time of the first "significant" rise in the pressure.[10] Each computed time was measured from the corresponding pressure versus time plot as described previously.[9] The ignition delay time represented a pressure rise of about 3 to 6 percent over the initial value. The thermodynamic data used for all computations are from the NASA Lewis data base, which is part of the Gordon and McBride Chemical Equilibrium Code.[14] New, improved data for many aromatic species were kindly provided by Bonnie J. McBride of this laboratory.

Turbulent Flow Reactor

As described previously,[9] the turbulent flow reactor was modeled as a constant pressure homogeneous batch reaction. A detailed description of the reactor is given by Hautman,[15] who indicates that the reactor was run at a constant pressure of 1 atm. In this apparatus fuel is injected into a nitrogen-diluted, highly turbulent stream of oxygen. The exact zero of reaction time is unknown and was taken as the point of fuel injection into the hot oxidant stream. Distance profiles were converted to time profiles by use of the measured flow velocities in the reactor.

RESULTS AND DISCUSSION

Comparison of Computed and Experimental Ignition Delay Times

Comparisons of experimental and computed ignition delay times are shown for four different starting mixtures in Figs. 1 to 4, where logarithm of ignition delay time is plotted against the reciprocal of temperature. Initial conditions are given in Table IV along with a comparison of computed and experimental results for all data points. Included in Table IV is an error analysis of the results. The percent difference between each experimental and computed ignition delay time is given along with the percent standard deviation defined previously[9] for each of the four sets of experimental conditions.

Figures 1 to 4 show fair to good agreement between computed and experimental results, better for the stoichiometric mixtures than for the lean mixture. Shown are the individual computed and experimental points as well as least-squares lines for each set of points, fitted to the empirical equation

$$\tau = A\ e^{\Delta E/RT}$$

where τ is the ignition delay time (experimental or computed), R is the universal gas constant and ΔE is the activation energy term for each set of initial conditions. For mixtures 1, 2, and 4, with initial pressures around 2 atm, the computed temperature dependence is weaker than that observed experimentally. For mixture 3, the dilute stoichiometric mixture with initial pressures around 6 atm, the computed temperature dependence is stronger than that observed experimentally. Computed and experimental activation energies are tabulated in Table V. The experimental activation energy for mixture 3 is significantly lower than that for mixture 2, whereas the computed activation energy for mixture 3 is only slightly lower than the value for mixture 2.

This experimental result is quite different from that for benzene-oxygen ignitions,[9] which had very similar initial shock conditions to those for the toluene experiments. For benzene neither the experimental nor the computed temperature dependences changed with initial pressure. In fact both the experimental and computed benzene-oxygen activation energies changed only moderately for all four initial mixtures used.

A comparison of ignition delay time measurements for mixtures 2 and 4 shows the effect of argon dilution for a constant equivalence ratio of 1.0. Figure 5 shows computed and experimental results for these two mixtures. Only the least-squares lines from Figs. 2 and 4 are shown for clarity. Our computed results can be seen to satisfactorily match the magnitude of the experimentally observed effect of argon dilution. In our previous benzene mixture computations,[9] the computed effect of argon dilution was much smaller than the experimentally observed effect.

A comparison of results for mixtures 2 and 3 shows the effect of increasing initial molar concentrations by shock-heating of the same molar mixture at two different initial pressures, 2 and 6 atm. The least-squares lines of Figs. 2 and 3 are replotted in Fig. 6, which shows that the computed magnitude of this concentration effect matches the experimental magnitude better at low temperatures than at high temperatures.

In summary, these comparisons have shown that our proposed toluene oxidation mechanism reasonably matches the experimental ignition delay time data over a wide range of initial conditions. The agreement between computation and experiment is about the same as that obtained for benzene mixtures in our previous study.[9]

Comparison of Computed and Experimental Turbulent Reactor Results

The turbulent-reactor toluene oxidation experiments were performed at essentially constant temperature, and no temperature versus time profile was reported.[3] The maximum measured temperature rise was reported to be 5 K in all experiments. As stated previously, we adjusted the rate coefficient parameters of reaction 1 so that the computed maximum temperature rise at the outlet of the reactor agreed with the experimental value.

Figures 7 to 14 show computed and experimental composition versus time profiles for toluene oxidation in the flow reactor with initial temperature of 1180 K and a pressure of 1 atm. Two mixtures, with equivalence ratios (φ) of $\varphi = 0.63$ and 1.4, were used in the experimental study and each mixture contained 0.14 mol % toluene. Figure 7 shows toluene versus time profiles for both mixtures. The computed profile for $\varphi = 0.63$ matches the experimental profile well, except toward the end of the reaction. Reasonable agreement is also obtained for the $\varphi = 1.4$ mixture, for which the maximum difference is about 15 percent. For both mixtures there is satisfactory agreement between experimental and computed slopes of the curves at early reaction times. This prediction of the fuel versus time profile contrasts with the failure to accurately predict a benzene destruction profile measured in the same reactor. Our benzene oxidation mechanism[9] predicts much more rapid destruction of benzene than is observed experimentally. Prediction of other concentration profiles was not as successful. The computed phenol profile (Fig. 9) for $\varphi = 1.4$ gives fair quantitative matching to the experimental profile. However, the computed profile for $\varphi = 0.63$ and the other computed profiles for cresols (Fig. 8), benzene (Fig. 10), benzaldehyde (Fig. 11), carbon monoxide (Fig. 12), benzyl alcohol (Fig. 13), and bibenzyl (Fig. 14) show only qualitative agreement with the experimental profiles. This qualitative agreement has been obtained even though there is little experimental information available about the reactions of many of these species. Several attempts were made to improve the overall agreement of the species profiles by certain rate coefficient variations. However, it was found that the single changes improved some profiles and made others worse. The results given appear to be the best compromise using the given set of reactions.

In summary, our proposed mechanism reasonably predicts the destruction profile of toluene, but is only partially successful in matching other experimental concentration profiles.

CONCLUDING REMARKS

We have presented a detailed toluene oxidation mechanism which reasonably computed measured ignition delay times in argon-diluted mixtures over a wide range of experimental conditions. In addition, the mechanism computed fairly good toluene versus time concentration profiles for the nitrogen-diluted oxidation in a turbulent flow reactor. Profiles of several other species concentrations were qualitatively matched.

Sensitivity analysis shows that the direct reaction of toluene with molecular oxygen strongly effects the profiles of temperature, pressure, and many species concentrations. This is in sharp contrast to the unimportance of the corresponding reaction in the benzene oxidation. A comparison of the heat of reaction for the benzene plus oxygen reaction (~60 kcal/mol) with that for the toluene plus oxygen reaction (~35 kcal/mol) justifies the much lower activation energy and higher rate coefficients for the latter reaction. Computations show that the molar rate of the toluene-oxygen reaction is always several orders of magnitude greater than that of the benzene-oxygen reaction for similar temperature and molar concentration conditions. The much higher reactivity of toluene with oxygen accounts for this reaction's being a major path for toluene oxidation. The benzyl-molecular oxygen reaction was found to be quite unimportant in toluene oxidation. This contrasts with the dominant effect of the corresponding phenyl-oxygen reaction in the oxidation of benzene. These facts are consistent with the idea that benzyl radical is conjugatively stabilized[1] and is less reactive than phenyl radical. The benzyl reaction with molecular oxygen is endothermic, whereas the corresponding phenyl reaction is very exothermic. The latter reaction, with its much higher rate coefficient and molecular rate, is one of the most important reactions in benzene oxidation, whereas the benzyl-oxygen reaction has very little effect on toluene oxidation. Because benzyl is a relatively stable radical, its reactions with other radicals, primarily hydroperoxyl, are its important ones in the oxidation of toluene.

A rate coefficient expression for the toluene-molecular oxygen reaction was found which predicted the temperature dependence of ignition delay times at high temperature (1300 to 1600 K) and also matched the very small temperature rise reported for the turbulent reactor at 1180 K. The results of this study have given a toluene oxidation mechanism that can be used for ignition and combustion modeling in practical, well-mixed combustion systems.

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TABLE I. - TOULENE OXIDATION MECHANISM

Number	Reaction	A CGS units[a]	n	E cal/mol	Reference
1	$C_7H_8 + O_2 \rightleftharpoons C_6H_5CH_2 + HO_2$	3.30×10^{14}	0.0	38 000	This work
2	$C_7H_8 \rightleftharpoons C_6H_5CH_2 + H$	4.45×10^{12}		72 600	4
3	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$	8.91×10^{12}		72 600	4
4	$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3$	4.00×10^{13}		5 120	4
5	$H + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2$	1.20×10^{14}		8 220	5
6	$H + C_7H_8 \rightleftharpoons C_6H_4CH_3 + H_2$	2.51×10^{14}		16 000	4
7	$CH_3 + C_7H_8 \rightleftharpoons C_6H_5CH_2 + CH_4$	4.37×10^{-4}	5.0	8 300	
8	$CH_3 + C_7H_8 \rightleftharpoons C_6H_4CH_3 + CH_4$	4.37×10^{-4}	5.0	12 300	
9	$C_6H_4CH_3 \rightleftharpoons C_4H_3 + C_3H_4$	1.00×10^{16}	0.0	82 000	
10	$C_6H_4CH_3 \rightleftharpoons C_3H_3 + 2\ C_2H_2$	1.00×10^{16}	0.0	83 000	
11	$C_6H_5CH_2 \rightleftharpoons C_3H_3 + 2\ C_2H_2$	1.78×10^{14}	0.0	84 800	
12	$CH_3 + C_6H_6 \rightleftharpoons CH_4 + C_6H_5$	4.37×10^{-4}	5.0	12 300	
13	$M + C_3H_4 \rightleftharpoons C_3H_3 + H$	2.00×10^{17}	0.0	65 000	
14	$H + C_3H_4 \rightleftharpoons C_3H_3 + H_2$	6.92×10^{14}		14 500	
15	$O + C_7H_8 \rightleftharpoons OHC_7H_7$	2.20×10^{13}		3 800	Adj from 7
16	$OH + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2O$	3.00×10^{12}		3 000	Adj from 8
17	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5CHO + H$	1.20×10^{13}		-------	Adj from 3
18	$C_6H_5CH_2 + O_2 \rightleftharpoons C_7H_7O + O$	6.30×10^{12}		43 000	3
19	$OH + C_7H_7OH \rightleftharpoons C_7H_7O + H_2O$	1.00×10^{13}		5 000	Estimated
20	$C_6H_5CH_2 + OH + M \rightleftharpoons C_7H_7OH + M$	1.00×10^{17}		-------	Estimated
21	$C_6H_5CH_2 + HO_2 \rightleftharpoons C_7H_7O + OH$	3.60×10^{12}		-------	Adj from 3
22	$C_7H_7O \rightleftharpoons C_6H_5CHO + H$	1.00×10^{12}		-------	3
23	$C_6H_5CHO \rightleftharpoons C_6H_5 + HCO$	1.00×10^{16}		82 000	Estimated

[a]Parameters in the expression $k = AT^n \exp(-E/RT)$.

TABLE I. - Concluded.

Number	Reaction	A CGS units	n	E cal/mol	Reference
24	$2\ C_6H_5CH_2 \rightleftharpoons C_{14}H_{14}$	1.00×10^{14}	0.0	-------	Estimated
25	$OHC_7H_7 + H_2 \rightleftharpoons C_6H_5OH + CH_4$	4.00×10^{11}		5 000	
26	$2\ C_6H_5 \rightleftharpoons C_{12}H_{10}$	1.00×10^{12}		-------	
27	$C_6H_5CHO + O_2 \rightleftharpoons C_6H_5CO + HO_2$	5.00×10^{12}		35 000	
28	$C_6H_5CHO + OH \rightleftharpoons C_6H_5CO + H_2O$	5.00×10^{12}		5 000	
29	$C_6H_5CHO + HO_2 \rightleftharpoons C_6H_5CO + H_2O_2$	1.00×10^{14}		5 000	
30	$C_6H_5CO \rightleftharpoons C_6H_5 + CO$	4.00×10^{14}		29 400	16
31	$C_6H_6 + O_2 \rightleftharpoons C_6H_5 + HO_2$	6.31×10^{13}		60 000	8
32	$C_6H_6 \rightleftharpoons C_6H_5 + H$	5.00×10^{15}		108 000	17
33	$C_6H_6 + H \rightleftharpoons C_6H_5 + H_2$	2.50×10^{14}		16 000	2
34	$C_6H_6 + O \rightleftharpoons C_6H_5 + OH$	2.78×10^{13}		4 910	7
35	$C_6H_6 + OH \rightleftharpoons C_6H_5 + H_2O$	2.13×10^{13}		4 580	18
36	$C_4H_3 + M \rightleftharpoons C_4H_2 + H + M$	3.31×10^{51}	-10.0	63 000	2
37	$C_6H_5O \rightleftharpoons C_5H_5 + CO$	2.51×10^{11}	0.0	43 900	19
38	$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	4.50×10^{12}		15 000	9
39	$C_6H_5 \rightleftharpoons C_4H_3 + C_2H_2$	1.58×10^{15}		82 000	2
40	$C_6H_5OH \rightleftharpoons C_6H_5O + H$	6.00×10^{13}		88 000	9
41	$C_5H_6 + O \rightleftharpoons C_5H_5O + H$	5.00×10^{12}		10 000	
42	$C_6H_5OH + OH \rightleftharpoons C_6H_5O + H_2O$	8.00×10^{12}		5 000	
43	$C_6H_5 + C_6H_6 \rightleftharpoons C_6H_5 + C_5H_6$	2.00×10^{11}		10 000	
44	$C_5H_5O + M \rightleftharpoons C_4H_5 + CO + M$	7.59×10^{13}		15 000	
45	$C_5H_5 + O_2 \rightleftharpoons C_5H_5O + O$	2.00×10^{12}		20 000	
46	$C_4H_5 \rightleftharpoons C_2H_3 + C_2H_2$	1.40×10^{13}		32 900	
47	$H + O_2 \rightleftharpoons OH + O$	1.66×10^{14}		16 400	20

TABLE II. - PRESSURE SENSITIVITY COEFFICIENTS FOR SHOCK IGNITION OF TOLUENE-OXYGEN-ARGON MIXTURES

Number	Reaction	Normalized pressure sensitivity coefficient, $A/p\ (\partial p/\partial A)$	
		$\varphi = 0.331$, $T = 1334$ K	$\varphi = 1.0$, $T = 1535$ K
1	$C_7H_8 + O_2 \rightleftharpoons C_6H_5CH_2 + HO_2$	0.02506	0.02423
2	$C_7H_8 \rightleftharpoons C_6H_5CH_2 + H$	-0.00258	-0.00056
3	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$	-0.00282	0.00068
4	$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3$	-0.00461	-0.00391
5	$H + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2$	-0.00396	-0.00763
15	$O + C_7H_8 \rightleftharpoons OHC_7H_7$	-0.00959	-0.00659
16	$OH + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2O$	-0.00762	-0.00493
17	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5CHO + H$	0.00842	0.00732
18	$C_6H_5CH_2 + O_2 \rightleftharpoons C_7H_7O + O$	0.00005	0.00009
20	$C_6H_5CH_2 + OH + M \rightleftharpoons C_7H_7OH + M$	-0.00107	0.00013
21	$C_6H_5CH_2 + HO_2 \rightleftharpoons C_7H_7O + OH$	0.01733	0.02058
23	$C_6H_5CHO \rightleftharpoons C_6H_5 + HCO$	0.00209	0.00402
29	$C_6H_5CHO + HO_2 \rightleftharpoons C_6H_5CO + H_2O_2$	0.00601	0.00106
38	$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	0.00734	0.00974
45	$C_5H_5 + O_2 \rightleftharpoons C_5H_5O + O$	0.01251	0.00869
47	$H + O_2 \rightleftharpoons OH + O$	0.01057	0.01286

TABLE III(a). - SENSITIVITY COEFFICIENTS OF FOUR SPECIES IN A TURBULENT FLOW REACTOR AT EQUIVALENCE RATIO 0.63

[Temperature = 1180 K; reaction time = 55 msec.]

Number	Reaction	Normalized sensitivity coefficient of species concentration c A/c (∂c/∂A)			
		Toluene	Cresols	Phenol	Benzene
1	$C_7H_8 + O_2 \rightleftharpoons C_6H_5CH_2 + HO_2$	-0.2143	0.4324	0.4815	0.1362
2	$C_7H_8 \rightleftharpoons C_6H_5CH_2 + H$	0.0416	0.2706	-0.2041	-0.3026
3	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$	0.0129	-0.0507	-0.0574	-0.0255
4	$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3$	0.0342	-0.2437	-0.4312	0.7074
5	$H + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2$	-0.0082	-0.4349	0.5212	-0.1585
15	$O + C_7H_8 \rightleftharpoons OHC_7H_7$	-0.0101	0.3538	-0.1150	-0.1512
16	$OH + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2O$	-0.0366	-0.2223	-0.0858	0.1251
17	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5CHO + H$	-0.0016	-0.2145	0.1175	0.1552
18	$C_6H_5CH_2 + O_2 \rightleftharpoons C_7H_7O + O$	-0.0002	0.0011	0.0008	0.0005
20	$C_6H_5CH_2 + OH + M \rightleftharpoons C_7H_7OH + M$	0.0016	0.0183	0.0354	0.0379
21	$C_6H_5CH_2 + HO_2 \rightleftharpoons C_7H_7O + OH$	-0.1438	0.1514	0.3644	0.2152
23	$C_6H_5CHO \rightleftharpoons C_6H_5 + HCO$	-0.0016	0.0543	0.0906	0.0755
25	$OHC_7H_7 + H_2 \rightleftharpoons C_6H_5OH + CH_4$	0.0091	-0.1617	0.1740	-0.0231
29	$C_6H_5CHO + HO_2 \rightleftharpoons C_6H_5CO + H_2O_2$	-0.0681	0.2788	0.0959	-0.0876
35	$C_6H_6 + OH \rightleftharpoons C_6H_5 + H_2O$	-0.0131	0.1782	0.1280	-0.3712
38	$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	-0.0238	0.1207	0.1272	0.0069
45	$C_5H_5 + O_2 \rightleftharpoons C_5H_5O + O$	-0.0253	0.1377	0.2049	0.0719
47	$H + O_2 \rightleftharpoons OH + O$	-0.0562	0.3721	-0.0152	-0.1576

TABLE III(b). - SENSITIVITY COEFFICIENTS OF FOUR SPECIES IN A TURBULENT FLOW REACTOR AT EQUIVALENCE RATIO 0.63

[Temperature = 1180 K; reaction time = 55 msec.]

Number	Reaction	Normalized sensitivity coefficient of species concentration c $A/c\ (\partial c/\partial A)$			
		Benzaldehyde	Carbon monoxide	Benzyl alcohol	Bibenzyl
1	$C_7H_8 + O_2 \rightleftharpoons C_6H_5CH_2 + HO_2$	0.4180	0.6536	0.6280	0.1349
2	$C_7H_8 \rightleftharpoons C_6H_5CH_2 + H$	-0.0890	0.1193	-0.0686	-0.3255
3	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$	-0.0141	-0.0564	-0.0074	0.0252
4	$H + C_7H_8 \rightleftharpoons C_6H_6 + CH_3$	-0.0752	-0.2625	-0.1130	0.1202
5	$H + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2$	0.0230	-0.0271	-0.0010	0.1926
15	$O + C_7H_8 \rightleftharpoons OHC_7H_7$	-0.2460	-0.1817	-0.0761	0.1424
16	$OH + C_7H_8 \rightleftharpoons C_6H_5CH_2 + H_2O$	0.0769	-0.1558	-0.4884	0.4777
17	$C_6H_5CH_2 + O \rightleftharpoons C_6H_5CHO + H$	0.2867	0.1470	0.0461	-0.1727
18	$C_6H_5CH_2 + O_2 \rightleftharpoons C_7H_7O + O$	0.0009	0.0006	0.0002	-0.0007
20	$C_6H_5CH_2 + OH + M \rightleftharpoons C_7H_7OH + M$	-0.0212	0.0136	0.5145	-0.1224
21	$C_6H_5CH_2 + HO_2 \rightleftharpoons C_7H_7O + OH$	0.8072	0.3246	0.3505	-0.0163
23	$C_6H_5CHO \rightleftharpoons C_6H_5 + HCO$	-0.0792	0.0778	-0.0102	-0.0744
25	$OHC_7H_7 + H_2 \rightleftharpoons C_6H_5OH + CH_4$	-0.0144	-0.0234	-0.0138	0.0212
29	$C_6H_5CHO + HO_2 \rightleftharpoons C_6H_5CO + H_2O_2$	-0.3922	0.3123	0.2812	0.1544
35	$C_6H_6 + OH \rightleftharpoons C_6H_5 + H_2O$	0.0397	0.1488	-0.0413	-0.1053
38	$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	0.0324	0.1268	0.0215	-0.0500
45	$C_5H_5 + O_2 \rightleftharpoons C_5H_5O + O$	0.0457	0.2177	0.0658	-0.0767
47	$H + O_2 \rightleftharpoons OH + O$	0.1125	0.0804	0.1464	0.0278

TABLE V. - COMPARISON OF COMPUTED AND EXPERIMENTAL ACTIVATION ENERGIES FOR TOLUENE-OXYGEN-ARGON IGNITION DELAY TIMES

Mixture description	Activation energy, cal/mol		Percent difference
	Experimental	Computed	
No. 1: φ = 0.331 P ≅ 2 atm	61850	43010	-30.4
No. 2: φ = 1.0, 95% Ar P ≅ 2 atm	61770	53210	-13.9
No. 3: φ = 1.0, 95% Ar P ≅ 6 atm	38790	46940	21.0
No. 4: φ = 1.0, 85% Ar P ≅ 2 atm	53260	41020	-23.0

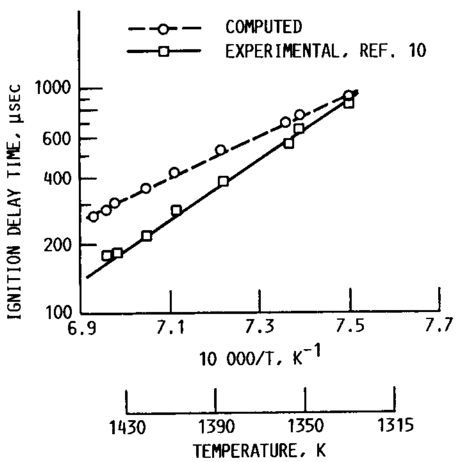

FIGURE 1. - IGNITION DELAY TIME VERSUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; MIXTURE 1, EQUIVALENCE RATIO = 0.331, INITIAL PRESSURE ≅ 2 ATM.

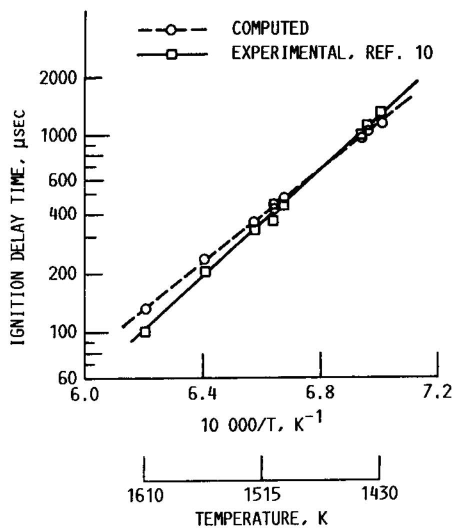

FIGURE 2. - IGNITION DELAY TIME VERSUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; MIXTURE 2: EQUIVALENCE RATIO = 1.0, 95 PERCENT AR, INITIAL PRESSURE ≅ 2 ATM.

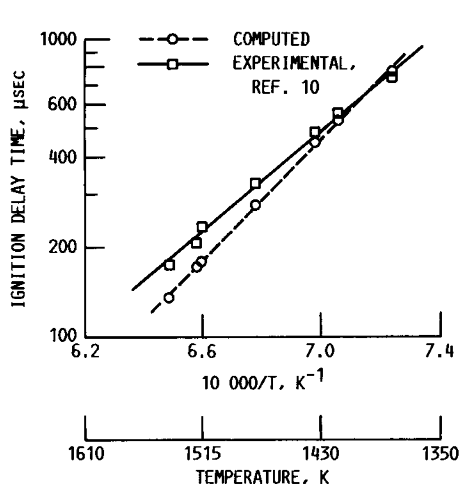

FIGURE 3. - IGNITION DELAY TIME VERSUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; MIXTURE 3: EQUIVALENCE RATIO = 1, 95 PERCENT AR, INITIAL PRESSURE ≅ 6 ATM.

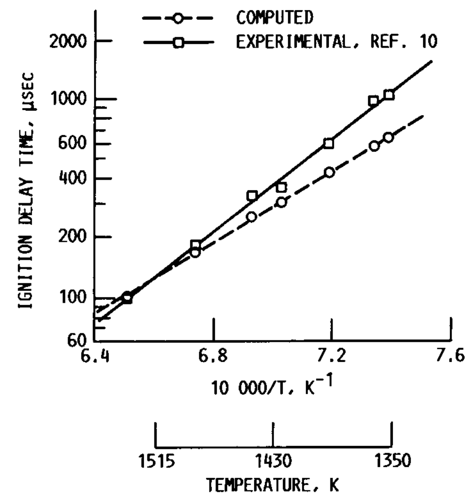

FIGURE 4. - IGNITION DELAY TIME VERSUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; MIXTURE 4: EQUIVALENCE RATIO = 1.0, 85 PERCENT AR INITIAL PRESSURE ≅ 2 ATM.

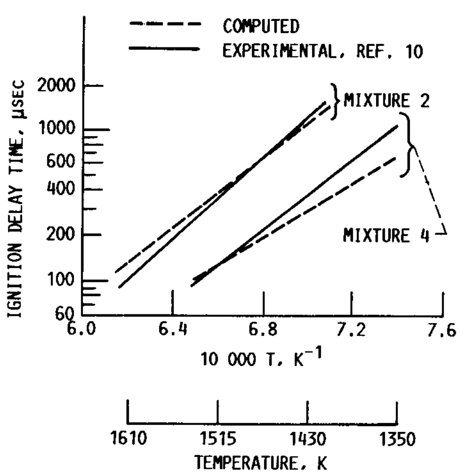

FIGURE 5. - IGNITION DELAY TIME VESUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; EFFECT OF ARGON DILUTION FOR EQUIVALENCE RATIO = 1.0: MIXTURE 2, 95 PERCENT AR; MIXTURE 4, 85 PERCENT AR; INITIAL PRESSURE ≅ 2 ATM.

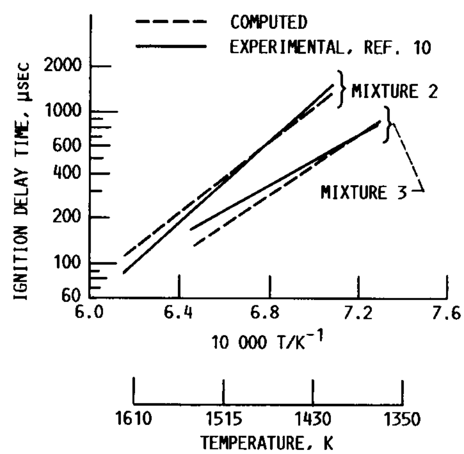

FIGURE 6. - IGNITION DELAY TIME VERSUS RECIPROCAL OF TEMPERATURE FOR TOLUENE-OXYGEN-ARGON; EFFECT OF INITIAL REACTANT MOLAR CONCENTRATION: EQUIVALENCE RATIO = 1.0. MIXTURE 2: 95 PERCENT AR; INITIAL PRESSURE ≅ 2 ATM. MIXTURE 3: 95 PERCENT AR; INITIAL PRESSURE ≅ 6 ATM.

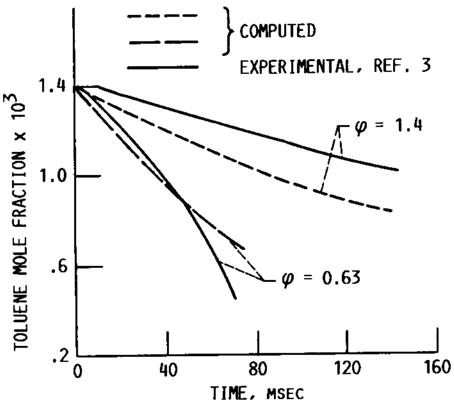

FIGURE 7. - TOLUENE VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

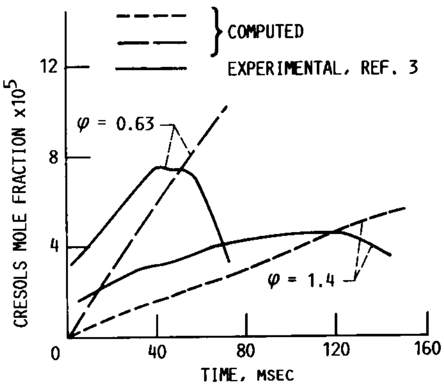

FIGURE 8. - CRESOLS VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

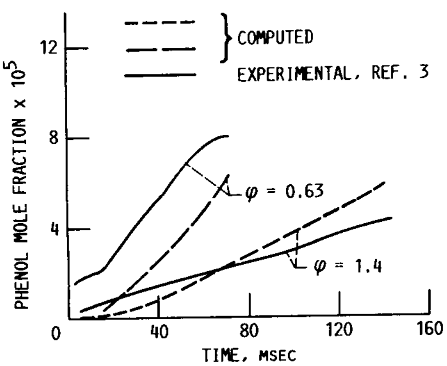

FIGURE 9. - PHENOL VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

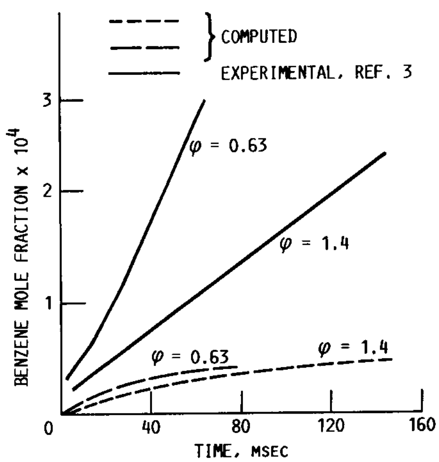

FIGURE 10. - BENZENE VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

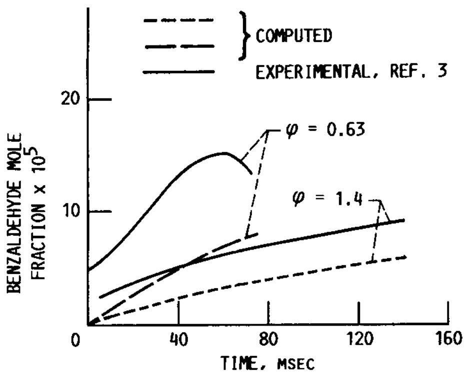

FIGURE 11. - BENZALDEHYDE VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

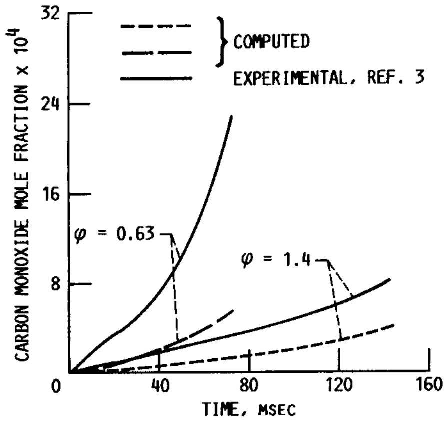

FIGURE 12. - CARBON MONOXIDE VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

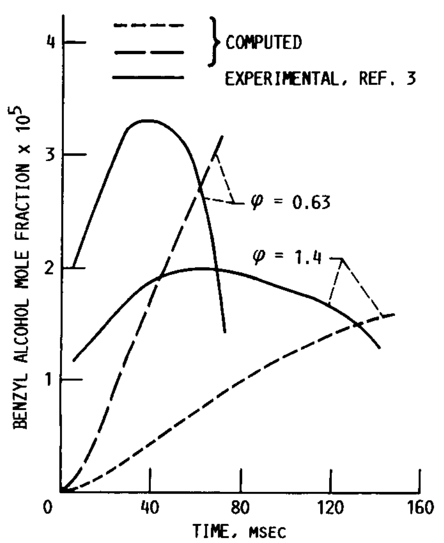

FIGURE 13. - BENZYL ALCOHOL VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

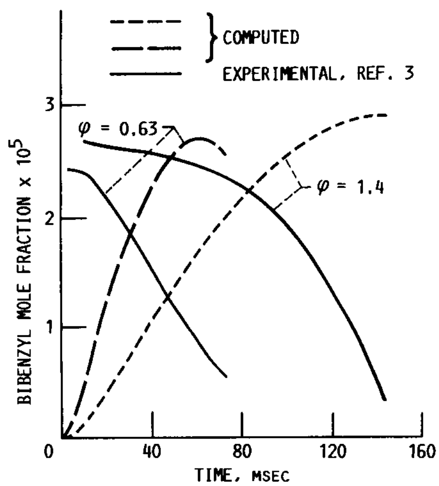

FIGURE 14. - BIBENZYL VERSUS TIME PROFILES FOR TOLUENE-OXYGEN REACTION IN NITROGEN. p = 1 ATM, T = 1180 K.

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16. Abstract

A detailed mechanism for the oxidation of toluene in both argon and nitrogen diluents is presented. The mechanism was used to compute experimentally measured ignition-delay times for shock-heated toluene-oxygen-argon mixtures with reasonably good success over a wide range of initial temperatures and pressures. Attempts to compute experimentally measured concentration profiles for toluene oxidation in a turbulent reactor were partially successful. An extensive sensitivity analysis was performed to determine the reactions which control the ignition process and the rates of formation and destruction of various species. The most important step was found to be the reaction of toluene with molecular oxygen, followed by the reactions of hydroperoxyl and oxygen atom with benzyl radical. These findings contrast with the benzene oxidation, where the benzene-molecular oxygen reaction is quite unimportant and the reaction of phenyl with molecular oxygen dominates. In the toluene mechanism the corresponding reaction of benzyl radical with oxygen is unimportant. Two reactions which are important in the oxidation of benzene also influence the oxidation of toluene for several conditions. These are the oxidations of phenyl and cyclopentadienyl radicals by molecular oxygen. The mechanism presented successfully computes the decrease of toluene concentration with time in the nitrogen-diluted turbulent reactor. This fact, in addition to the good prediction of ignition delay times, shows that this mechanism can be used for modeling the ignition and combustion process in practical, well-mixed combustion systems.

17. Key Words (Suggested by Author(s)) Modeling and simulation; Aromatic oxidation; Chemical mechanisms; Kinetics	18. Distribution Statement Unclassified - Unlimited; Subject Category 25

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